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XXIV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

GENERAL CONSIDERATIONS IN REGARD TO CERTAIN COMPOUNDS PREPARED FROM BROMNITROBENZOLS.

By C. Loring Jackson.

Presented May 28, 1889.

Several compounds derived from various bromnitrobenzols have been described recently by me in conjunction with other chemists in a number of papers * from this laboratory, but in the course of the work certain general observations were made in regard to them which could not conveniently be introduced in the separate papers, and are therefore collected here.

The Action of Sodium Malonic (or Acetacetic) Ester on certain Bromnitrobenzols.

The actions studied were the following: —

Sodium Malonic Ester on
  Tribromtrinitrobenzol, $C_6Br_3(NO_2)_3$, melting point 285°.
  Tribromdinitrobenzol, $C_6HBr_3(NO_2)_2$, melting point 192°.
  Tetrabromdinitrobenzol, $C_6Br_4(NO_2)_2$, melting point 227°.
Sodium Acetacetic Ester on
  Tribromdinitrobenzol, $C_6HBr_3(NO_2)_2$, melting point 192°.

In all these cases the action was essentially the same, and may be represented by the following reactions for tribromtrinitrobenzol: —

$$\text{I. } C_6Br_3(NO_2)_3 + CHNa(COOC_2H_5)_2 = NaBr + C_6Br_2(NO_2)_3CH(COOC_2H_5)_2.$$

$$\text{II. } C_6Br_2(NO_2)_3CH(COOC_2H_5)_2 + CHNa(COOC_2H_5)_2 = C_6Br_2(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2.$$

$$\text{III. } C_6Br_2(NO_2)_3CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 = C_6HBr(NO_2)_3CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2.$$

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* These Proceedings, xxiii. 138; xxiv. 1, 105, 234, 256, 271, 288.

The formation of brommalonic ester in III., the only point in these reactions about which there was any doubt, was proved by the isolation of acetylentetracarbonic ester* or of tartronic acid† from the oily secondary product, as these substances could hardly have been formed otherwise than by the following reactions, —

$$CHBr(COOC_2H_5)_2 + CHNa(COOC_2H_5)_2 = CHCH(COOC_2H_5)_4 + NaBr.$$

$$CHBr(COOC_2H_5)_2 + NaOH = CHOH(COOC_2H_5)_2 + NaBr.$$

Reactions I.–III. are given because they show more clearly what has taken place, but the discussion which follows does not depend on them alone, since the analyses of the products are sufficient to prove that in all the cases studied the action has consisted in the replacement of one atom of bromine by the malonic ester radical, and of the second by hydrogen, while the third (and fourth) has remained unaltered.‡ This difference in the behavior of the three atoms of bromine is certainly very curious, and, so far as I can find, no case analogous to it has been described as yet. The strangeness of the replacement of bromine by hydrogen becomes especially evident when it is remembered that in every case there was a large excess of sodium malonic ester present, and that this second atom of bromine has therefore combined with the carbon of malonic ester (see Reaction III.) in preference to the sodium of sodium malonic ester, so that the tendency to introduce hydrogen rather than the malonic ester radical has been strong enough in this case to overcome the attraction of the bromine for the sodium, and to cause it to combine with carbon instead.

I have not succeeded in finding any explanation of these curious observations which satisfies me, but hope to be led to one by further experiment. It can be stated at present, however, that the difference of behavior in the three bromine atoms is not due to differences in their position on the benzol ring. This is shown easily in the case of the tribromtrinitrobenzol, as here the three atoms of bromine occupy exactly similar positions, each being ortho to two nitro groups and para to the third. In the tribromdinitrobenzol,§ also, the first and third atoms of bromine are similarly placed (ortho to one, para to the other nitro group), but the second (that replaced by hydrogen) is peculiar in being ortho to both nitro groups. It is evident, then, that in these reactions both similarly placed bromine atoms are not replaced by the malonic ester radical; but it is also to be observed that the bromine which is replaced by hydrogen has in every case stood in the ortho position to two nitro groups, and this suggested to me that perhaps an atom of bromine in this position might be especially susceptible to the action of free malonic ester. To test this hypothesis I mixed some tribromdinitrobenzol dissolved in benzol with malonic ester, and, after the mixture had stood for some time in the cold, warmed it for about an hour on the water bath, but even after this treatment no action* had taken place, as the tribromdinitrobenzol melted unaltered at 192°. This result was confirmed by a similar experiment with acetacetic ester, which stood with tribromdinitrobenzol for six months without any action. It is evident, therefore, that this atom of bromine is not attached in an especially loose way to the molecule, and that its replacement by hydrogen does not depend only on its position with reference to the nitro groups, but is due also to the presence of the malonic ester radical.

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* These Proceedings, xxiv. 265.

† Ibid., xxiv. 238.

‡ In the trinitro compound the third atom of bromine is replaced by the malonic ester radical to a limited extent even in the cold, but it is acted on much less easily than the first.

§ In the tetrabromdinitrobenzol the fourth atom of bromine seems to have no influence on the reaction, and therefore all I say about the tribromdinitrobenzol also applies to this substance.

On the Relative Ease with which the Reactions take Place.

This subject will I hope prove susceptible of quantitative treatment, and I propose next year to try some experiments of this sort; I shall therefore at present confine myself to two qualitative observations, which were so marked that a quantitative confirmation of them seems unnecessary.

The tribromtrinitrobenzol is distinctly more reactive than the tribromdinitro- or tetrabromdinitrobenzol, as it acts on alcoholic ammonia in the cold, whereas the other two must be heated to 100° in sealed vessels to bring about this reaction.

The sodium acetacetic ester acts much less energetically than sodium malonic ester upon tribromdinitrobenzol, since the red color of the product appears instantaneously with the malonic ester, but only after some time with acetacetic ester, and the yield of the acetacetic compound is much smaller than that of the malonic derivative, if the reactions are carried on under the same conditions.

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* The addition of a little aqueous sodic hydrate was enough to cause action at once, as shown by the appearance of the red color of the sodium salt.

On the Acidity of the substituted Malonic Esters, Acetacetic Ester, and Ketones described in the preceding Papers.

In order to determine the relative acidity of these substances, their action with the following reagents was studied: acid sodic carbonate, sodic carbonate, ammonic hydrate, sodic hydrate. Each reagent was added in aqueous solution to the solid organic substance, and, after observing what took place, alcohol was added, and any change in the behavior of the substance noted. All these experiments were tried at the same time, great care being used to make the conditions as nearly the same as possible. The results can be divided into those which were perfectly definite, that is, where the differences consisted in the fact that one compound formed a salt with the reagent, and another did not; and those depending to a certain extent upon my judgment, in which the differences were only in the amount of salt formed, as shown by the depth of color, or in the quantity of alcohol necessary to produce the salt. The differences of the first class can be described most clearly and succinctly by the following table, in which the substances are arranged in the order of their acidity, beginning with the most acid. The columns correspond to the reagents, and the word "Salt" indicates that a salt was formed, as shown by the color imparted to the solution, or solid.

	$NaHCO_3$		Na_2CO_3		NH_4OH		NaOH	
	Aqueous.	With Alcohol.	Aqueous.	With Alcohol.	Aqueous.	With Alcohol.	Aqueous	With Alcohol.
I. $C_6H_2Br(NO_2)_2C_2H_3OCH_2CO_2C_2H_5$	Salt	Salt	Salt	Salt	Salt	Salt	Salt	Salt
II. $C_6HBr(NO_2)_3CH(CO_2C_2H_5)_2$	Salt	Salt	Salt	Salt	Salt	Salt	Salt	Salt
III. $C_6H_2Br(NO_2)_2CH(CO_2C_2H_5)_2$	..	Salt	Salt	Salt	Salt	Salt	Salt	Salt
IV. $C_6H_2Br(NO_2)_2CH_2COCH_3$	..	Salt	*	Salt	Salt	Salt	Salt	Salt
V. $C_6HBr_2(NO_2)_2CH(CO_2C_2H_5)_2$	..	Salt	Salt	Salt	Salt	Salt	Salt	Salt
VI. $C_6H_2C_6H_5NH(NO_2)_2CH(CO_2C_2H_5)_2$	..	Salt	..	Salt	..	Salt	..	Salt
VII. $C_6HBrC_6H_5NH(NO_2)_2CH(CO_2C_2H_5)_2$	..	..	..	Salt	..	Salt	..	Salt
VIII. $C_6H_2C_6H_5NH(NO_2)_2CH_2COCH_3$	..	..	..	Salt	..	..	..	Salt

* No salt was obtained from IV. with aqueous sodic carbonate, but I ascribe this to a mistaken observation, probably due to the difficulty in moistening the ketone with the aqueous solution.

The observations recorded in this table divide these substances into the following groups (indicated by the lines): — I. and II., most acid; III., IV., and V., less acid; VI., less acid; VII., less acid; VIII., least acid. The relative acidity of I. and II. was determined by data of the second sort mentioned above, since I. gave a much stronger coloration than II. with aqueous sodic carbonate, ammonic hydrate, or sodic hydrate. The order of III., IV., and V. was determined by the following observations. With acid sodic carbonate and dilute alcohol, III. and IV. gave a stronger red color than V. With aqueous sodic carbonate, III. gave a pale red, V. a much paler, in fact barely perceptible color. With aqueous ammonic hydrate, III. gave a pale red, V. a very pale barely perceptible red, and IV. stood between III. and V. in color. With aqueous sodic hydrate, the color was confined to the crystals of the organic substance, owing to the slight solubility of the salt in a solution of sodic hydrate, and III. turned dark red, IV. pale red, while V. showed a mixture of pale red particles of the salt and white ones of the ester. Upon adding alcohol to the mixture of the substance and either aqueous sodic carbonate or ammonic hydrate, a dark red color was obtained from all three, but much more alcohol was necessary to produce this color with V. than with III. or IV. My observations on the intensity of the color with different reagents confirm the order of compounds VI., VII., and VIII., but I do not think it worth while to give the details. I should add, also, to show that the personal equation did not enter to any great extent into these observations, that the substances during the experiments were arranged in an order different from that of their acidity, and that the order of acidity given above derived from these experiments was a surprise to me in many particulars.

These experimental results justify the following inferences in regard to the effect of differences in composition upon the acidity of these substances.

(*a.*) The introduction of an additional nitro group (in the ortho position) increases the acidity, since II. is more acid than III.

(*b.*) The replacement of hydrogen (in the ortho position) by bromine diminishes the acidity, since V. is less acid than III.

(*c.*) The replacement of bromine (in the meta position) by the aniline radical C_6H_5NH reduces the acidity very considerably, since III., IV., and V. are much more acid than VI., VIII., and VII. respectively.

In all these cases the differences occur in the benzol ring, and the effects are very marked (especially in *c*) when it is considered that the hydrogen affected is attached to the side chain, and therefore more removed from the influence of the acid radicals than in most of the similar cases previously described, in which the element influenced was attached to the benzol ring. These observations recall some made by me several years ago, when I showed* that the ring bromine in the three brombenzylbromides had a marked influence in diminishing the ease with which the side-chain bromine was removed, varying with its position on the benzol ring, the para bromine having less influence than the meta, the meta than the ortho.

(*d.*) The nature of the side-chain also has a marked influence on the acidity; thus the substituted acetacetic ester I. is much more acid than the corresponding malonic ester III., a result in harmony with Claisen and Ehrhardt's† classification of the radicals according to their acid-producing power, since they give the following list beginning with that which has the least influence, "phenyl, carboxyl, benzoyl, acetyl, formyl." An approximate measure of the relative acid-producing power of carboxyl and acetyl is given by the comparison of III. and IV., which possess nearly the same degree of acidity, and therefore it follows that one acetyl has nearly, although not quite, the same effect as two carboxyls.

(*e.*) The comparison of a dimalonic with the corresponding monomalonic compound in this respect is of interest. Unfortunately I had none of the trinitrophenylendimalonic ester when the comparison described above was made, so that this substance does not appear in the table; but by comparing the observations made on it when its properties were studied with those on the bromtrinitrophenylmalonic ester, I have found that the dimalonic compound is much less acid than the brommonomalonic ester, since acid sodic carbonate in aqueous solution has no action upon it, and even aqueous sodic carbonate gives only a very faint red color.‡ This weaker acidity can be accounted for by the hypothesis, that the influence of the three nitro groups being divided between two malonic ester radicals, each will have the acidifying influence of only one and a half nitro groups, instead of the three, which act on the acid hydrogen in the monomalonic compound.

The stability of the salts of all these compounds is remarkable, the sodium salt even of the anilidodinitrobenzylmethylketone (the least acid of all these substances) having been prepared and analyzed with no especial difficulty; it shows therefore a marked difference in this respect from desoxybenzoine ($C_6H_5COCH_2C_6H_5$), the sodium compound of which, according to Victor Meyer,* has not been isolated. In fact, he thinks it probable that it may not exist in the free state, and leaves it doubtful whether the syntheses of homologues of desoxybenzoine are preceded by the formation of a sodium compound, as with malonic or acetacetic ester, or whether the homologue is formed direct by the removal of hydrogen and the halogen by sodic hydrate, according to this reaction:

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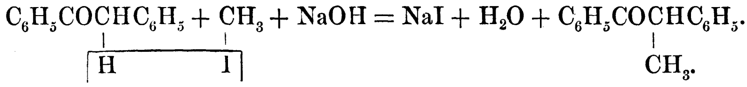
* These Proceedings, xvi. 241.

† Ber. d. ch. G. 1889, p. 1019.

‡ I should be inclined to place the trinitrophenylendimalonic ester between III. and V., although from the absence of comparative work its exact place cannot be determined with certainty; this, however, is of little importance, as the comparison of it with II. is the only one of especial interest.



$$C_6H_5CO\underset{\substack{|\\ H}}{C}HC_6H_5 + \underset{\substack{|\\ I}}{C}H_3 + NaOH = NaI + H_2O + C_6H_5CO\underset{\substack{|\\ CH_3.}}{C}HC_6H_5.$$

The reason for this striking difference in acidity between the substituted benzylmethylketones and desoxybenzoine can hardly be due to the fact that the former contain the more active acetyl instead of the benzoyl contained in the latter, although this may have some influence, but in my opinion is rather to be ascribed to the heightening of the acid-producing power of the phenyl by the nitro groups which it contains. The salts of the acetacetic or malonic esters are much more stable than those of the ketones, as was to be expected, since in these cases the hydrogen is exposed to the acidifying power of three radicals (nitrophenyl and two carboxyls, or one carboxyl and an acetyl), and their stability almost equals that of the salts of Bischoff's † orthonitrobenzoylmalonic ester, in which the nitrophenyl of my compounds is replaced by the even more acid nitrobenzoyl.

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* Ber. d. ch. G. 1888, p. 1291.

† Ann. Chem., ccli. 364.